

## Patent Abstracts of Japan

PUBLICATION NUMBER : 11172298  
PUBLICATION DATE : 29-06-99

APPLICATION DATE : 09-12-97  
APPLICATION NUMBER : 09338583

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INT.CL. : C11D 17/06 C11D 3/10 C11D 3/20 C11D 3/37 C11D 3/60 //(C11D 3/60 , C11D 3:37 , C11D 3:20 , C11D 3:10 )

TITLE : TABLET TYPE DETERGENT AND PREPARATION THEREOF

ABSTRACT : PROBLEM TO BE SOLVED: To obtain accelerated dissolution by effervescence of carbon dioxide when soaked in water and excellent mechanical strength in a dry state by compression-molding a detergent composition comprising a detergent particle containing a detergent activating compound and a builder, a water soluble polymer, an organic acid and a carbonate thereby forming a detergent with a specific macro porosity.

SOLUTION: Macro porosity is preferably 15% or more. The objective detergent is, for example, obtained by dry-blending a detergent particle, a water soluble polymer compd., an organic acid and a carbonate and compression- molding by means of tablet molding or the like while adjusting macro porosity, melting the water soluble polymer compd. by heat and subsequently cooling thereby causing the water soluble polymer compd. to bind. The pressure in compression molding is preferably 1-30 kgf/cm<sup>2</sup>. Preferably the composition comprises 60-95 wt.% of the detergent particle, 1-10 wt.% of the water soluble polymer compd., 2-15 wt.% of the organic acid and 2-15 wt.% of the carbonate.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a tablet mold detergent and its manufacture approach. It is related with the tablet mold detergent which dissolves promptly, and its manufacture approach in more detail, foaming to carbon dioxide gas underwater.

[0002]

[Description of the Prior Art] Conventionally, the tablet mold detergent is manufactured compression or by carrying out eburation in detergent powder. since a tablet mold detergent does not have the need for measuring -- handling -- easy -- moreover, \*\* -- since it is not high, there is an advantage that it is compact, and storage space is small and ends.

[0003] However, it does not have mechanical strength sufficient by dryness, but the conventional tablet mold detergent has the fault of collapsing and being hard to dissolve, even if it is a time of getting wet.

[0004] Then, as a tablet mold detergent which can cancel this fault, a carbonate or a bicarbonate, and an organic acid are blended, and when dipped in water, the tablet mold detergent with which the dissolution is promoted is proposed by foaming of carbon dioxide gas (JP,62-30197,A, JP,58-105910,A, JP,62-89616,A).

[0005] However, the tablet mold detergent which blended these carbonates or bicarbonates, and organic acids has the fault that time lag is for water to advance and foam to the interior of a tablet, although a tablet front face contacts water and foams underwater. When a tablet mold detergent contacts water, in order that components, such as an activator, may check gelation thru/or that form a \*\*-strike and water advances [ components, such as this activator gelled thru/or pasted ] into the interior on the front face, the cause requires time amount for the reaction inside a tablet, and is not to fully acquire the effectiveness of promotion of the dissolution by foaming.

[0006] When it fabricates so that it may collapse easily and it may dissolve, and a tablet may have high voidage with low compression moulding pressure even if a front face does not gel underwater or it gels in order to cancel these faults, the tablet mold detergent obtained runs short of mechanical strengths, and has the fault of being inferior to handling nature.

[0007]

[Problem(s) to be Solved by the Invention] So that this invention may be made in view of said conventional technique, an organic acid may be mixed with a carbonate or a bicarbonate in a tablet mold detergent and a carbonate or a bicarbonate, and an organic acid may react promptly also inside a tablet (foaming) It aims at offering the tablet mold detergent which the dissolution was promoted by foaming of carbon dioxide gas when dipped in water by giving high voidage so that water might advance easily underwater, and was excellent in the mechanical strength in dryness.

[0008]

[Means for Solving the Problem] Namely, this invention (1) The detergent particle containing a detergent activity compound and a builder, It comes to press the detergent constituent containing a water soluble polymer compound, an organic acid, and a carbonate. The tablet mold detergent characterized by having 15% or more of macro voidage, (2) The tablet mold detergent of the aforementioned (1) publication which has 18% or more of total voidage, (3) The above (1) which is at least one sort chosen from the group which an organic acid becomes from a citric acid, a succinic

acid, a tartaric acid, a fumaric acid, a malic acid, and oxalic acid, or a tablet mold detergent given in (2), (4) aforementioned (1) - (3) which is at least one sort chosen from the group which a carbonate becomes from a sodium carbonate, potassium carbonate, a sodium hydrogencarbonate, and a potassium hydrogencarbonate -- either -- the tablet mold detergent of a publication -- (5) aforementioned (1) - (4) whose water soluble polymer compound is the polyethylene glycol which has weight average molecular weight 1300-20000 -- either -- the tablet mold detergent of a publication -- (6) A detergent constituent 60 - 95 % of the weight of detergent particles, 1 - 10 % of the weight of water soluble polymer compounds, aforementioned (1) - (5) containing 2 - 15 % of the weight of organic acids, and 2 - 15 % of the weight of carbonates -- either -- the tablet mold detergent of a publication -- And (7) The detergent particle containing a detergent activity compound and a builder, It is a detergent constituent containing a water soluble polymer compound, an organic acid, and a carbonate A pressure 1 - 30 kgf/cm<sup>2</sup> It is related with the manufacture approach of a tablet mold detergent of having 15% or more of macro voidage characterized by pressing.

[0009]

[Embodiment of the Invention] As described above, the tablet mold detergent of this invention presses the detergent constituent containing a detergent activity compound, the detergent particle containing a builder and a water soluble polymer compound, an organic acid, and a carbonate, and is obtained, and the big description is in the point that the point of having 15% or more of macro voidage and said water soluble polymer compound, the organic acid, and the carbonate are used.

[0010] By having 15% or more of macro voidage, the tablet mold detergent of this invention is excellent in the permeability of water, collapses easily with the carbon dioxide gas which occurs in neutralization of an organic acid and a carbonate further, and discovers the property to excel in the solubility over water remarkably.

[0011] Only by generally, adjusting so that the macro voidage of a tablet mold detergent may only merely become 15% or more, although a porous tablet mold detergent with voidage high to be sure is obtained, since the mechanical strength of a tablet mold detergent falls, the handling is difficult.

[0012] Then, in order to raise a mechanical strength, when compression molding is carried out with high pressure, the permeability of the water of a tablet mold detergent falls conversely.

[0013] On the other hand, it is adjusted so that macro voidage may become 15% or more, but the tablet mold detergent of this invention has the mechanical strength excellent in dryness at the same time it holds the outstanding solubility over water by using the water soluble polymer compound for the detergent constituent which constitutes the tablet mold detergent.

[0014] In addition, the macro voidage said to this specification means the rate that the opening between the detergent particles contained in the tablet mold detergent occupies to the volume of said whole tablet mold detergent here. The measuring method of this macro voidage is mentioned later.

[0015] The detergent particle used for this invention contains a detergent activity compound and a builder, as described above.

[0016] As said detergent activity compound, the Nonion activator, an anion activator, a both-sexes activator, and a cation activator are raised.

[0017] As an example of said detergent activity compound, for example Polyoxyethylene alkyl ether, Polyoxyethylene alkyl phenyl ether, polyoxyethylene sorbitan fatty acid ester, Polyoxyethylene sorbitol fatty acid ester, polyethylene glycol fatty acid ester, Polyoxyethylene polyoxypropylene alkyl ether, polyoxyethylene castor oil, Polyoxyethylene hydrogenated castor oil, polyoxyethylene alkylamine, A glycerine fatty acid ester, a higher-fatty-acid alkanol amide, alkyl glycoside, The Nonion activators, such as an alkylamine oxide; Alkylbenzene sulfonates, Alkyl ether sulfate, an alkenyl ethereal sulfate salt, alkyl sulfate, An alkenyl sulfate, alpha-olefin sulfonate, alpha-sulfo fatty-acid salt, Both-sexes activators, such as anion activator; carbobetaine, such as alpha-sulfo fatty-acid-ester salt, alkyl ether carboxylate, alkenyl ether carboxylate, and soap, and sulfobetaine; although cation activators, such as Ji long-chain mold quarternary ammonium salt, etc. are raised This invention is not limited only to this instantiation. In addition, said detergent activity compound is independent, or two or more sorts can usually be mixed and used for it.

[0018] HLB[Griffin (Griffin) of said detergent activity compound -- as for value] called for by law, it is desirable 5-17 from a viewpoint of excelling in a detergency, and that it is 8-14 preferably.

[0019] moreover -- the inside of said Nonion activator -- a carbon number -- 10-20 -- desirable -- 10-

15, the straight chain that are 12-14 still more preferably, or branched chain -- having -- the number of ethyleneoxide average addition mols -- 5-15 -- 6-12, and the polyoxyethylene alkyl ether that is 6-10 still more preferably are preferably desirable.

[0020] Although said polyoxyethylene alkyl ether generally contains the alkyl ether of the number of ethyleneoxide low addition mols so much, it is desirable for the amount of a 0-3-mol addition product to be 25 or less % of the weight preferably 35 or less % of the weight.

[0021] In order that adjusting so that it may be preferably contained 5% of the weight or more 3% of the weight or more in a detergent particle in order to give sufficient detergency may give sufficient solubility desirably, as for the amount of said detergent activity compound, it is desirable to adjust so that it may be preferably contained 60 or less % of the weight 65 or less % of the weight in a detergent particle.

[0022] An inorganic builder and an organic builder are raised as a builder used for this invention.

[0023] As said inorganic builder, for example A sodium carbonate, potassium carbonate, Sodium bicarbonate, a sodium sulfite, sodium sesquicarbonate, a sodium silicate, On the silicate compound and concrete target which have 100-500 (CaCO<sub>3</sub> mg/g) preferably, more than ion-exchange ability 100 (CaCO<sub>3</sub> mg/g) It passes. Alkaline salts, such as KISUTO-Tokuyama make and trade name:SKS-6, Neutral salt, such as a sodium sulfate, orthophosphate, a pyrophosphate, tripolyphosphate, a metaphosphate -- passing -- phosphate, such as KISAME thalline acid chloride and a phytic acid salt, -- The Europe patent application public presentation No. 550,048 specifications (1993), such as alkali-metal salts, such as sodium salt and potassium salt, and a silicate compound given in JP,64-41116,B, General formula:  $x_1$  and (M<sub>2</sub> O) aluminum 2O<sub>3</sub>,  $y_1$  (SiO<sub>2</sub>), and  $w_1$  (H<sub>2</sub> O)

(In M, alkali-metal atoms, such as sodium and a potassium,  $x_1$ ,  $y_1$ , and  $w_1$  show the number of mols of each component among a formula. Generally)  $x_1$  The number of 0.7-1.5, and  $y_1$  The number of 0.8-6, and  $w_1$  the positive number of arbitration -- being shown -- the crystalline aluminosilicate, and general formula: $x_2$  and (M<sub>2</sub> O) aluminum 2O<sub>3</sub> which are expressed,  $y_2$  (SiO<sub>2</sub>), and  $w_2$  (H<sub>2</sub> O)

(In M, a sodium atom or a potassium atom,  $x_2$ ,  $y_2$ , and  $w_2$  show the number of mols of each component among a formula. Generally)  $x_2$  The number of 0.7-1.2, and  $y_2$  The number of 1.6-2.8, and  $w_2$  the positive number of 0 or other arbitration -- being shown -- the amorphism aluminosilicate expressed -- General formula:  $x_3$  (M<sub>2</sub> O) and aluminum 2O<sub>3</sub>,  $y_3$  (SiO<sub>2</sub>),  $z_3$  (P<sub>2</sub> O<sub>5</sub>), and  $w_3$  (among a formula) (H<sub>2</sub> O) M is a sodium atom or a potassium atom,  $x_3$ ,  $y_3$ , and  $z_3$ . And  $w_3$  shows the number of mols of each component.  $x_3$  The number of 0.20-1.10, and  $y_3$  The number of 0.20-4.00, and  $z_3$  The number of 0.001-0.80, and  $w_3$  the positive number of 0 or arbitration -- being shown -- the amorphism aluminosilicate expressed is raised. Especially in said crystalline aluminosilicate, the crystalline aluminosilicate expressed with general formula:Na<sub>2</sub> O-aluminum<sub>2</sub> O<sub>3</sub>,  $y_4$ , and (SiO<sub>2</sub>)  $w_4$  H<sub>2</sub> O ( $y_4$  and  $w_4$  show the number of mols of each component among a formula,  $y_4$  shows the number of 1.8-3.0, and  $w_4$  shows the number of 1-6) is desirable.

[0024] In said inorganic builder, sodium tripolyphosphate, a sodium carbonate, an aluminosilicate, and especially the silicate compound that has more than ion-exchange ability 100 (CaCO<sub>3</sub> mg/g) are desirable.

[0025] As said organic builder, for example Moreover, ethane -1, 1-diphosphonic acid, Ethane -1, 2-triphosphonic acid, and ethane-1-hydroxy - 1 and 1-diphosphonic acid and those derivatives, Ethanehydroxy-1,1,2-triphosphonic acid, ethane -1, 2-dicarboxy - 1, 2-diphosphonic acid, Phosphonate, such as methane hydroxy phosphonic acid; 2-phosphono butane -1, 2-dicarboxylic acid, 1-phosphono butane - Phosphono carboxylate; aspartic acids, such as 2, 3, 4-tricarboxylic acid, and alpha-methyl phosphono succinic acid, Amino acid salts, such as glutamic acid; A nitrilotriacetic acid salt, an ethylenediaminetetraacetic acid salt, Amino poly acetate, such as diethylenediamine 5 acetate; Polyacrylic acid, Polyacrylate, Pori aconitic acid, the Pori itaconic acid, the Pori citraconic acid, The Pori fumaric acid, a polymer lane acid, the poly meta contest acid, a Polly alpha-hydroxy acrylic acid, A polyvinyl phosphonic acid, sulfonation polymer lane acid, and maleic-anhydride-diisobutylene copolymer, A maleic-anhydride-styrene copolymer, a maleic-anhydride-methyl-vinyl-ether copolymer, A maleic-anhydride-ethylene copolymer, a maleic-anhydride-ethylene bridge formation copolymer, A maleic-anhydride-vinyl acetate copolymer, a maleic-anhydride-acrylonitrile copolymer, A maleic-anhydride-acrylic ester copolymer, a maleic-anhydride-butadiene copolymer, A maleic-anhydride-isoprene copolymer, the Polly beta-keto carboxylic acid guided from a maleic

anhydride and a carbon monoxide, An itaconic-acid-ethylene copolymer, an itaconic-acid-aconitic acid copolymer, An itaconic-acid-maleic-acid copolymer, an itaconic-acid-acrylic-acid copolymer, A malonic-acid-methylene copolymer, an itaconic-acid-fumaric-acid copolymer, an ethylene glycol-ethylene terephthalate copolymer, A vinyl-pyrrolidone-vinyl acetate copolymer, 1-butene - 2, 3, a 4-tricarboxylic acid-itaconic-acid-acrylic-acid copolymer, The polyester, the poly aldehyde carboxylic acid which have quaternary ammonium, Cis--isomer [ of an epoxy succinic acid ], Pori [N, and N-screw (carboxymethyl) acrylamide], Pori (hydroxy acid), DEMBU disuccinic acid ester, a maleate, Terephthalic-acid ester, starch phosphoric ester, dicarboxy starch, Polyelectrolytes, such as dicarboxy methyl starch, a carboxymethyl cellulose, and succinate; A polyethylene glycol, Non-dissociating high molecular compounds, such as polyvinyl alcohol, a polyvinyl pyrrolidone, and cold-water fusibility urethane-ized polyvinyl alcohol; Diglycolic acid, Oxy-disuccinic acid, carboxymethyl malic acid (CMOS), Cyclopentane - 1, 2, 3, 4-tetracarboxylic acid, tetrahydrofuran - 1, 2, 3, 4-tetracarboxylic acid, Tetrahydrofuran - 2, 2, 5, and 5-tetracarboxylic acid, a citric acid, Carboxymethyl ghosts, such as a lactic acid, a tartaric acid, cane sugar, a lactose, and a raffinose, The carboxymethyl ghost of pentaerythritol, the carboxymethyl ghost of a gluconic acid, A condensate with polyhydric alcohol or a saccharide, a maleic anhydride, or a succinic anhydride, A condensate with hydroxy acid, a maleic anhydride, or a succinic anhydride, Benzene polycarboxylic acid, ethane which are represented with a merit acid - 1, 1, 2, and 2-tetracarboxylic acid, Ethene - 1, 1, 2, and 2-tetracarboxylic acid, butane - 1, 2, 3, 4-tetracarboxylic acid, Propane - 1, 2, 3-tricarboxylic acid, butane -1, 4-dicarboxylic acid, Oxalic acid, a sulfo succinic acid, Deccan -1, 10-dicarboxylic acid, sulfotricarbaric acid, A sulfo itaconic acid, a citric acid, a malic acid, oxy-disuccinic acid, a gluconic acid, Monsanto Industrial Chemicals company company make, a trade name: Organic-acid salts, such as Builder M, etc. are raised. In these organic builders, citrate, polyacrylate, and polyethylene glycols, such as citric-acid 3 sodium, are desirable. In these organic builders, the polyethylene glycol of 2700-19000 is especially raised for citric-acid 3 sodium, sodium polyacrylate, and weight average molecular weight (from the hydroxyl value measured according to JIS K 1557 6.4 to calculation) as a desirable thing. Said builder is independent, or mixes two or more sorts and is usually used.

[0026] From a viewpoint which demonstrates granulation nature and ion-exchange ability effective at the time of use (at the time of underwater distribution), as for said builder's mean particle diameter, it is desirable that they are 0.5 micrometers or more and 1 micrometers or more of \*\*\*\*\* , and it is desirable that they are 500 micrometers or less and 400 micrometers or less of \*\*\*\*\* .

[0027] In order that adjusting so that it may be preferably contained 40% of the weight or more 35% of the weight or more in a detergent particle in order to give sufficient detergency may give sufficient solubility desirably, as for said builder's amount, it is desirable to adjust 97 or less % of the weight, so that it may be contained 95 or less % of the weight preferably.

[0028] Although the detergent particle used for this invention contains said detergent activity compound and builder, it may coat this detergent particle with surface coating agents, such as an enzyme and a zeolite, as occasion demands.

[0029] The detergent particle used for this invention may be the mixture of the particle of each component which constitutes this detergent particle, and may be a particle obtained by corning the mixture containing a detergent activity compound and a builder.

[0030] Mean particle diameter uses a thing 150 micrometers or more as a principal component, and as for the content of the particle which is less than 150 micrometers, it is desirable [ as for said detergent particle ] that particle diameter is 5 or less % of the weight, when raising the macro voidage of the tablet mold detergent of this invention. In addition, in order that the mean particle diameter of said detergent particle may raise the moldability of a tablet mold detergent and may raise the mechanical strength of the tablet mold detergent obtained, it is desirable that they are 2000 micrometers or less and 1500 micrometers or less of \*\*\*\*\* .

[0031] In this invention, although said not all detergent particles need to have uniform particle diameter, since the particle size distribution of this detergent particle equalizes Sharp, that the distribution width of face of particle size distribution is small if it puts in another way makes the opening of detergent particles equalize, it is easy and control of the macro voidage of the tablet mold

detergent obtained becomes easy, it is desirable. When the particle size distribution of this detergent particle is log normal distribution, it is desirable for the standard deviation when carrying out the volume plot of the particle size distribution of a detergent particle with a rosin RAMURA graph to be 2.0 or less.

[0032] In addition, said standard deviation is formula: (standard deviation) = (84.3-% of the weight particle size) / (50-% of the weight particle size).

It can ask "Be alike."

[0033] the tablet mold detergent with which the bulk density of said detergent particle is obtained --

\*\* -- in order to make it not become high and to raise compactability -- 0.5 g/cm<sup>3</sup> the above --

desirable -- 0.7 g/cm<sup>3</sup> It is desirable that it is above.

[0034] In this invention, since water fully permeates even the interior, and collapses with the carbon dioxide gas which occurs in neutralization by the organic acid and the carbonate and solubility is raised even if the front face of this tablet mold detergent gels when the tablet mold detergent of this invention is thrown in underwater, it is necessary to secure the approach route of water. Therefore, in this invention, in order that a macro opening (opening between detergent particles) may prepare in a tablet mold detergent and \*\*\*\* may secure this macro opening, a water soluble polymer compound is used.

[0035] When the tablet mold detergent of this invention is dipped in water, in order for water to fully permeate and to make it collapse easily as said water soluble polymer compound, in ordinary temperature (about 20 degrees C), it is powdered and a solid-state or the thing which presents water solubility and has the melting point of 40-100 degrees C is desirable.

[0036] As an example of said water soluble polymer compound, a polyethylene glycol, a polyvinyl pyrrolidone, water-soluble polyacrylate, polyvinyl alcohol, etc. are raised, for example. In these, a polyethylene glycol can be suitably used in this invention. In this polyethylene glycol, it is JISK.

1557 Especially the thing that has the weight average molecular weight 1300-20000 computed from the hydroxyl value measured by the pyridine phthalic anhydride method according to 6.4 is

desirable. The polyethylene glycol which has said weight average molecular weight 1300-20000 is JIS. K When the melting point is measured by congealing-point \*\*\*\*\* indicated by 8001 "reagent test-method general notices", it has the melting point of 40-100 degrees C.

[0037] There is no limit in the approach of adding a water soluble polymer compound to a detergent particle, and especially the approach of mixing a water soluble polymer compound and a detergent particle. Moreover, the distributed condition of the water soluble polymer compound contained in a tablet mold detergent may be uniform, and may be uneven. About these, it specifically mentions later.

[0038] As an example of said organic acid, a citric acid, a succinic acid, a tartaric acid, a fumaric acid, a malic acid, the oxalic acid that is a solid-state at about 20 degrees C (ordinary temperature) are raised, for example.

[0039] Moreover, as an example of said carbonate, a sodium carbonate, potassium carbonate, a sodium hydrogencarbonate, a potassium hydrogencarbonate, etc. are raised, for example. Especially in these, the combination of the point of the amount of foaming per unit mass to a citric acid and a sodium hydrogencarbonate is desirable.

[0040] In order to give sufficient washing capacity, 60% of the weight or more, as for the amount of the detergent particle contained in said detergent constituent, it is desirable that it is 70 % of the weight or more preferably, and it is desirable that it is 85 or less % of the weight preferably 95 or less % of the weight in consideration of the point which blends other components.

[0041] As for the amount of the water soluble polymer compound contained in said detergent constituent, it is desirable that it is 3 % of the weight or more preferably 1% of the weight or more in order to fully raise the mechanical strength of the tablet mold detergent obtained, and in order to give sufficient macro opening for the tablet mold detergent obtained, it is desirable that it is 8 or less % of the weight preferably 10 or less % of the weight.

[0042] In order to make it fully collapse by foaming, it is desirable that it is 5 % of the weight or more preferably 2% of the weight or more, respectively, and in order that the amount of the organic acid contained in said detergent constituent and the amount of a carbonate may enable it to fully blend a washing component, it is desirable [ an amount ] respectively that it is 12 or less % of the

weight preferably 15 or less % of the weight.

[0043] Next, the manufacture approach of the tablet mold detergent of this invention is explained.

[0044] As an example of representation of the manufacture approach of the tablet mold detergent of this invention, the dryblend of a detergent particle, a water soluble polymer compound, an organic acid, and the carbonate is carried out, for example, and the method of pressing with making tablet shaping etc. for example, heating the obtained detergent constituent, adjusting macro voidage, carrying out melting of the water soluble polymer compound, making it cool subsequently, making a water soluble polymer compound bind, and manufacturing a tablet mold detergent etc. is raised.

[0045] In case the dryblend of said detergent particle, a water soluble polymer compound, an organic acid, and the carbonate is carried out, as a powder-mixing machine, it can pass and for example, a high speed mixer, a REDIGE mixer, and things usually used, such as a NSHIERU mixer, a ribbon mixer, and a NAUTA mixer, can be used.

[0046] The pressure at the time of pressing with making tablet shaping etc. is 1 kgf/cm<sup>2</sup>, in order to give the suitable mechanical strength for the tablet mold detergent obtained. They are 5 kgf/cm<sup>2</sup> preferably above. In order considering as the above is desirable, and it prevents collapse of a detergent particle and to secure predetermined macro voidage, it is 30 kgf/cm<sup>2</sup>. They are 20 kgf/cm<sup>2</sup> preferably hereafter. Considering as the following is desirable. In this invention, the macro voidage of the tablet mold detergent obtained can be adjusted to a predetermined value by adjusting this pressure.

[0047] Therefore, in this invention, it is desirable to carry out measuring of the relation between the pressure at the time of pressing beforehand and macro voidage by approaches, such as a method of mercury penetration.

[0048] In addition, since micro voidage may also change to coincidence at this time, measuring is desirable.

[0049] Here, said micro voidage means the rate that the detailed opening where the detailed opening included in the detergent particle before compression molding itself is included in the detergent particle in the rate of occupying in this detergent particle, or the obtained tablet mold detergent itself occupies in this tablet detergent. When the volume of the detailed opening in a detergent particle is set to  $dV$  and the volume of \*\*\*\* and a tablet mold detergent is specifically set to  $V_t$  for the volume of a detergent particle, the micro voidage of a detergent particle is expressed with  $dV/****$ , and the micro voidage of a tablet mold detergent is expressed with  $dV/V_t$ .

[0050] In addition, especially in this invention, if there is no notice, said micro voidage will say the micro voidage in a tablet mold detergent.

[0051] If the detergent constituent containing the detergent particle containing a detergent activity compound and a builder, a water soluble polymer compound, an organic acid, and a carbonate is pressed, since the pore diameter of the micro opening before compression molding (opening which the detergent particle itself has) changes delicately, said micro voidage will come to change with the pressures at the time of this compression molding. Therefore, it is desirable to newly measure the micro voidage of said tablet mold detergent.

[0052] The average pore diameter of the micro opening measured with a method of mercury penetration is usually 10 micrometers or less.

[0053] Said macro voidage is usually expressed with the difference of the total voidage of a tablet mold detergent, and micro voidage.

[0054] In addition, since a detergent particle collapses and the macro opening (opening between detergent particles) of the tablet mold detergent obtained is lost when the pressure at the time of compression molding is too much high, it is not desirable.

[0055] The average pore diameter of said macro opening is usually about 1-200 micrometers, when it measures with a method of mercury penetration.

[0056] As for the temperature when heating the Plastic solid which pressed with making tablet shaping etc. and was acquired, it is desirable that it is more than the melting point of a water soluble polymer compound in order to raise the mechanical strength of the tablet mold detergent which is made to bind detergent particles and is obtained, and in order to prevent deterioration by heating, it is desirable that it is 20 degrees C or less.

[0057] By said approach, it presses with making tablet shaping etc. so that macro voidage may serve



as a predetermined value, and since actuation of subsequently carrying out heating melting of the water soluble polymer compound is taken, there is an advantage that it can adjust easily so that macro voidage may serve as a predetermined value.

[0058] When adopting said approach, as contrasted with the approach of heating before shaping which a water soluble polymer compound mentions later, it may become so much required, and the mechanical strength of the tablet mold detergent which will be obtained if mixing with a detergent particle and a water soluble polymer compound is not fully performed may become small locally.

[0059] In addition, in this invention, a detergent particle and an organic acid may be beforehand coated with a water soluble polymer compound for example, a high speed mixer, a REDIGE mixer, and by passing and mixing a detergent particle, a water soluble polymer compound, and an organic acid using the usual powder-mixing machines, such as a NSHIERU mixer. In this case, after carrying out heating melting of the water soluble polymer compound beforehand, spraying this water soluble polymer compound on a detergent particle and an organic acid, and adding this water soluble polymer compound in the state of powder, and mixing, heating melting may be carried out and you may coat. A carbonate can be added after this actuation and it can mix.

[0060] When said approach is adopted, there is an advantage that the mechanical strength of the tablet mold detergent there is not only an advantage that mixing of a detergent particle, a water soluble polymer compound, and an organic acid and melting of a water soluble polymer compound can be performed to coincidence, but obtained as contrasted with the case where it heats after shaping becomes high. Since the coat of the water soluble polymer compound is furthermore carried out also to an organic acid and contact of an organic acid and a carbonate is barred, the reaction of both by absorption of moisture is controlled and there is an advantage that the stability of a product increases.

[0061] If it presses with making tablet shaping etc., with melting of the water soluble polymer compound carried out in adopting said approach, since a water soluble polymer compound will flow and a macro opening will be filled, the alignment error of macro voidage becomes large. Therefore, in adopting said approach, after coating a detergent particle and an organic acid with a water soluble polymer compound, it is desirable to present compression molding, such as making tablet shaping, as it once cools and subsequently being described above.

[0062] In addition, since it may decompose under heating, and a carbonate may generate carbon dioxide gas and water and may spoil the stability of a final product, it is desirable to shorten the processing time under heating of a carbonate as much as possible.

[0063] It is made to dissolve in solvents, such as water, and a water soluble polymer compound is used, and when making it dry, it is not desirable in order that an organic acid and a carbonate may cause the debasement of a lifting and a final product for neutralization.

[0064] There is no limitation especially in the configuration of the tablet mold detergent obtained in this way, for example, a cylindrical shape and a cube form are begun, and it is JIS. K The configuration currently raised to description "the configuration of a table 1 granulation object and a name" of 8841 "a granulation object strength test method" is raised.

[0065] The washing activity compound of the amount needed for an average washing may be contained in said one tablet mold detergent, and you may make it become the amount needed for an average washing by containing the washing activity compound of an amount smaller than a complement in the average washing, and using some tablet mold detergents. Usually, it is preferably suitable for the weight of one tablet mold detergent that they are [ 5-60g ] 10-30g.

[0066] Since it has 18% or more, and excels in a mechanical strength in dryness and collapses easily in a damp or wet condition 15% or more preferably, macro voidage can use the tablet mold detergent of this invention suitable for washing of the washing etc., for example. In addition, for said macro voidage, bulk density is 3 0.5g/cm. Even if compression molding of the above detergent particle is carried out, in order to make it have sufficient mechanical strength, it is desirable that it is 35% or less preferably 40% or less.

[0067] Moreover, for the total voidage expressed as the sum of macro voidage and micro voidage in this invention, since micro voidage is also required to some extent in order to secure the solubility of the detergent particle itself, it is desirable that it is 20% or more preferably 18% or more, and bulk density is 0.5 g/cm<sup>3</sup>. Even if compression molding of the above detergent particle is carried out, in



order to make it have sufficient mechanical strength, it is desirable that it is 40% or less preferably 50% or less.

[0068]

[Example] Next, although this invention is further explained to a detail based on an example, this invention is not limited only to this example.

[0069] The example 1 of manufacture [manufacture of a detergent particle]

In a REDIGE mixer [path clearance 5.0mm of made in Matsusaka Research Institute, the capacity of 20l., an impeller, and a container wall] as a builder -- zeolite 4A mold [particle-size [ primary / an average of ]: -- the 3 micrometer]20 weight section -- sodium-carbonate [particle-size [ primary / an average of ]: -- the 290 micrometer]36 weight section and crystalline silicate -- [ -- the product made from KISUTO -- As the SKS-6]4 weight section and an oil absorption agent, Trade name : Amorphism aluminosilicate [0.8Na<sub>2</sub>O-aluminum<sub>2</sub>O<sub>3</sub> and 6.5SiO<sub>2</sub>, Oil absorption:245ml / , and 3 / 100g, pore volume specific-surface-area [ of 310cm<sup>3</sup> / of 153m<sup>2</sup> ] 2 / g, and 100g]10 weight section was supplied, and stirring of a main shaft [200rpm] and a chopper [4000rpm] was started.

[0070] In said REDIGE mixer, as a detergent activity compound Next, Nonion activator [polyoxyethylene dodecylether, The number of ethyleneoxide average addition mols : It supplies melting point:15-degree-C]30 weight applying [ 8 and ] them for 1 minute. as the surface lining agent after stopping stirring after 4-minute progress -- a zeolite -- the 4A mold [particle-size [ primary / an average of ]:3-micrometer]15 weight section was supplied, stirring was performed for 30 seconds, subsequently it discharged from said REDIGE mixer, and the detergent particle was obtained.

[0071] In addition, said Lady GEMIKISAHE's total charge was 4kg.

[0072] Next, it is JIS about the bulk density and mean particle diameter of a detergent particle which were obtained. K It investigated according to the approach of measuring by the approach specified to 3362, and showing those micro voidage below, and those averages were calculated. Consequently, the bulk density of the obtained detergent particle was [ 420 micrometers and the micro voidage of 0.85g / ml / /and mean particle diameter ] 12%.

[0073] [Micro voidage in a detergent particle] The true density of a detergent particle is JIS. M According to 8717 "an iron ore density measurement approach 5. air comparison method", it can measure by changing a Measuring condition in part.

[0074] Since the detergent particle used as a sample is constituted including moisture from the first at this time, it is not necessary to dry as specified in "5.3 Sample" of said JIS.

[0075] The volume of a detergent particle is JIS. M According to 8719 "an iron ore pellet-volumetry approach 5. mercury process", it can measure by changing a Measuring condition in part.

[0076] Since the detergent particle used as a sample is constituted including moisture from the first at this time, it is not necessary to dry as specified in "5.3 Sample" of said JIS. Moreover, the mass of a sample is JIS from the title between the accuracy of measurement. M It is desirable to be referred to as 60g like 8717 "an iron ore density measurement approach 5. air comparison method."

[0077] Furthermore, the porosity in a detergent particle is computed according to calculation approach" of JIS8716 iron-ore pellet-apparent density and porosity using the value of these true density and volume. Thus, the porosity measured and computed is the micro voidage in a detergent particle.

[0078] The example 2 of manufacture [manufacture of a detergent particle]

In a REDIGE mixer [path clearance:5.0mm of made in Matsusaka Research Institute, the capacity of 20l., an impeller, and a container wall] as a builder -- zeolite 4A mold [particle-size [ primary / an average of ]: -- 3 micrometer]20 weight section and sodium-carbonate [particle-size [ primary / an average of ]: -- the 290 micrometer]10 weight section -- As an oil absorption agent, the 0.8Na<sub>2</sub>O-aluminum<sub>2</sub>O<sub>3</sub> and 6.5SiO<sub>2</sub>, pore volume:310cm<sup>3</sup> / 100g, specific-surface-area:153m<sup>2</sup> / g, and amorphism aluminosilicate [oil absorption:245ml / 100g] 10 weight section, Zeolite 4A mold [primary [ an average of ] particle size : The 3 micrometer]25.8 weight section, the sodium-carbonate 10 weight section, Spray drying particle [bulk density which an average carbon number becomes from the fatty-acid sodium 2 weight section of 18, the carboxymethylcellulose sodium salt 0.1 weight section, and the moisture 1 weight section : 0.43g/ml Mean diameter: The 220 micrometer]25 weight section was supplied and stirring of a main shaft [200rpm] and a chopper

[4000rpm] was started.

[0079] In said REDIGE mixer, as a detergent activity compound Next, Nonion activator [polyoxyethylene dodecylether, The number of ethyleneoxide average addition mols : It supplies melting point:15-degree-C]10 weight applying [ 8 and ] them for 1 minute. as the surface lining agent after stopping stirring after progress for 4 minutes -- a zeolite -- the 4A mold [particle-size [ primary / an average of ]:3-micrometer]15 weight section was supplied, stirring was performed for 30 seconds, subsequently it discharged from said REDIGE mixer, and the detergent particle was obtained. In addition, the total charge to said REDIGE mixer was 4kg.

[0080] Next, the bulk density, mean particle diameter, and micro voidage of the obtained detergent particle were investigated like the example 1 of manufacture. Consequently, the bulk density of the obtained detergent particle was [ 440 micrometers and the micro voidage of 0.57g / ml //and mean particle diameter ] 20%. 570316

[0081] The detergent particle obtained in the example 1 - the example 1 of 5 manufactures, It supplies to the high speed mixer [the product made from Fukae Industry] of 10 liter capacity at a rate which shows a citric acid in Table 1 as a water soluble polymer compound as the polyethylene glycol [the Kao Corp. make] and organic acid of weight average molecular weight 7300-9300. Main shaft 200rpm, It mixed at the jacket temperature of 60 degrees C for 10 minutes by chopper 600rpm, and it supplied at a rate which shows a sodium hydrogencarbonate in Table 1 as a carbonate further, it mixed at the jacket temperature of 20 degrees C for 3 minutes by main shaft 200rpm and chopper 600rpm, and the detergent constituent was obtained.

[0082] Next, the obtained detergent constituent was cooled radiationally for 30 minutes, and it pressed by the pressure shown in Table 1, heated for 10 minutes at the temperature of 105 degrees C, subsequently it cooled radiationally for 30 minutes, and the tablet mold detergent was obtained.

[0083] As the detergent particle obtained in the example 6 - the example 1 of 7 manufactures, and a water soluble polymer compound, the polyethylene glycol of weight average molecular weight 7300-9300 [the Kao Corp. make], A sodium hydrogencarbonate is fed into the high speed mixer [the product made from Fukae Industrial] of 10 liter capacity as a citric acid and a carbonate as an organic acid at a rate shown in Table 1. It mixed at the jacket temperature of 25 degrees C for 10 minutes by main shaft 200rpm and chopper 600rpm, pressed by the pressure shown in Table 1, heated for 10 minutes at the temperature of 105 degrees C, subsequently it cooled radiationally for 30 minutes, and the tablet mold detergent was obtained.

[0084] As the detergent particle obtained in the example 2 of example of comparison 1 manufacture, and a water soluble polymer compound, it supplied to the high speed mixer [the product made from Fukae Industry] of 10 liter capacity at a rate that weight average molecular weight shows the polyethylene glycol [the Kao Corp. make] of 7300-9300 in Table 1, and it mixed for 10 minutes and at the jacket temperature of 60 degrees C by main shaft 200rpm and chopper 600rpm, and the detergent constituent was obtained.

[0085] Next, the obtained detergent constituent was cooled radiationally for 30 minutes, and it pressed by the pressure shown in Table 1, heated for 10 minutes at the temperature of 105 degrees C, subsequently it cooled radiationally for 30 minutes, and the tablet mold detergent was obtained.

[0086] As the detergent particle obtained in the example 2 of example of comparison 2 manufacture, and a water soluble polymer compound, the polyethylene glycol of weight average molecular weight 7300-9300 [the Kao Corp. make], It supplies to the high speed mixer [the product made from Fukae Industry] of 10 liter capacity at a rate which shows a citric acid in Table 1 as an organic acid. It mixed at the jacket temperature of 60 degrees C for 10 minutes by main shaft 200rpm and chopper 600rpm, and it supplied at a rate which shows a sodium hydrogencarbonate in Table 1 as a carbonate further, it mixed at the jacket temperature of 20 degrees C for 3 minutes by main shaft 200rpm and chopper 600rpm, and the detergent constituent was obtained.

[0087] Next, the obtained detergent constituent was cooled radiationally for 30 minutes, and it pressed by the pressure shown in Table 1, heated for 10 minutes at the temperature of 105 degrees C, subsequently it cooled radiationally for 30 minutes, and the tablet mold detergent was obtained.

[0088] As the detergent particle obtained in the example 3 of a comparison - the example 1 of 4 manufactures, and a water soluble polymer compound, the polyethylene glycol of weight average molecular weight 7300-9300 [the Kao Corp. make], It supplies to the high speed mixer [the product

made from Fukae Industry] of 10 liter capacity at a rate which shows a citric acid in Table 1 as an organic acid. It mixed at the jacket temperature of 60 degrees C for 10 minutes by main shaft 200rpm and chopper 600rpm, and it supplied at a rate which shows a sodium hydrogencarbonate in Table 1 as a carbonate further, it mixed at the jacket temperature of 20 degrees C for 3 minutes by main shaft 200rpm and chopper 600rpm, and the detergent constituent was obtained.

[0089] Next, the obtained detergent constituent was cooled radiationally for 30 minutes, and it pressed by the pressure shown in Table 1, heated for 10 minutes at the temperature of 105 degrees C, subsequently it cooled radiationally for 30 minutes, and the tablet mold detergent was obtained.

[0090] Weight average molecular weight as the detergent particle obtained in the example 1 of example of comparison 5 manufacture, and a water soluble polymer compound The polyethylene glycol of 7300-9300 [the Kao Corp. make], It supplies to the high speed mixer [the product made from Fukae Industry] of 10 liter capacity at a rate which it is shown in a citric acid as an organic acid, and shows a sodium hydrogencarbonate in Table 1 as a carbonate. It mixed at the jacket temperature of 25 degrees C for 10 minutes by main shaft 200rpm and chopper 600rpm, pressed by the pressure shown in Table 1, heated for 10 minutes at the temperature of 105 degrees C, subsequently it cooled radiationally for 30 minutes, and the tablet mold detergent was obtained.

[0091] As physical properties of the obtained tablet mold detergent, the micro voidage and all voidage, the macro voidage, collapse reinforcement, and dissolution time amount of a tablet mold detergent were investigated according to the following approaches. The result is shown in Table 1. (1) The micro voidage tablet mold detergent of a tablet mold detergent is unfolded carefully, and it separates carefully at a time one grain of primary particle which constitutes the tablet mold detergent. Although it is not necessary to perform this actuation strictly, the particle diameter of the separated primary particle should just be 2000 micrometers or less. Although the water soluble polymer compound contained in addition to the detergent particle may collapse at this time, it dissociates similarly [ without also leaving those fines ].

[0092] Thus, the unfolded primary particle is called a constituent particle. The micro voidage in this constituent particle turns into micro voidage of a tablet mold detergent.

[0093] The true density of a constituent particle is JIS. M According to 8717 "an iron ore density measurement approach 5. air comparison method", it can measure by changing a Measuring condition in part. Since it is constituted including moisture from the first, as it is in "5.3 Sample" of said JIS, it is not necessary to dry the constituent particle which serves as a sample at this time.

[0094] The volume of a constituent particle is JIS. M According to 8719 "an iron ore pellet-volumetry approach 5. mercury process", it can measure by changing a Measuring condition in part. Since the constituent particle which serves as a sample at this time is constituted including moisture from the first, as it is in "5.3 Sample" of said JIS, it does not need to dry. Moreover, the mass of a sample is JIS from the problem of the accuracy of measurement. M Being referred to as 60g is desirable like 8717 "an iron ore density measurement approach 5. air comparison method."

[0095] Furthermore, the value of these true density and volume is used and it is JIS about the porosity in a constituent particle. It computes according to M8716 "the calculation approach of iron ore pellet-apparent density and porosity." This actuation is performed about five samples, and maximum and the minimum value are omitted, and let the average of remaining three values be the micro voidage in a constituent particle. This value is the micro voidage of a tablet mold detergent.

(2) The total voidage of all the voidage tablet mold detergents of a tablet mold detergent is the following, and make and measure it.

[0096] The true density of a tablet mold detergent is JIS. M According to 8717 "an iron ore density measurement approach 5. air comparison method", it can measure by changing a Measuring condition in part. Since the tablet mold detergent which serves as a sample at this time is constituted including moisture from the first, as it is in "5.3 Sample" of said JIS, it does not need to dry.

[0097] The volume of a tablet mold detergent is JIS. M According to 9719 "an iron ore pellet-volumetry approach 5. mercury process", it can measure by changing a Measuring condition in part. Since the tablet mold detergent which serves as a sample at this time is constituted including moisture from the first, as it is in "5.3 Sample" of said JIS, it does not need to dry. Moreover, let the sample used for measurement be one tablet mold detergent.

[0098] Furthermore, the value of these true density and volume is used and it is JIS about the

porosity of a tablet mold detergent. M It computes according to 8716 "the calculation approach of iron ore pellet-apparent density and porosity."

[0099] Thus, the porosity measured and computed is the total voidage of a tablet mold detergent.

(3) Compute the macro voidage of the macro voidage tablet mold detergent of a tablet mold detergent as a difference of the total voidage of a tablet mold detergent, and the micro voidage of a tablet mold detergent.

(4) Collapse reinforcement JIS Z By 8841 "a granulation object strength test method 3.1 collapse strength test method", the collapse reinforcement of the diameter direction of a tablet mold detergent is measured.

(5) Feed 15g of tablet mold detergents obtained dissolution time into 2 tub type washing machine [Toshiba Make and a trade name:Galaxy 3.6VH-360SI mold] into which 30l. of 20-degree C tap water was put beforehand. Electrical conductivity is measured stirring for 20 minutes by making stirring reinforcement into a "criterion."

[0100] Measurement of electrical conductivity is Toa Electronics, Ltd. make and trade name:TOA. Conductivity Meter It carries out using CM-60SWO]. The saturation value (terminal point) of electrical conductivity measures electrical conductivity every 30 seconds, after starting stirring, and it makes it electrical conductivity in case the rate of change of the measured value at that time is 1% non-slot as contrasted with the last measured value. However, measurement of said electrical conductivity is performed for at least 5 minutes. In addition, it asks for the rate of the dissolution based on formula:[rate of the dissolution] =[(electrical conductivity of wash liquid in predetermined time)-(electrical conductivity of water before detergent injection)] /[(electrical conductivity saturation value of wash liquid)-(electrical conductivity of water before detergent injection)] x100.

[0101] Soluble evaluation is expressed with elapsed time until the rate of the dissolution becomes 90%. In addition, as for said time amount, it is desirable that it is less than for 300 seconds.

[0102]

[Table 1]

実施例 番号	洗剤組成物の組成 (重量部)				成形圧力 (kgf/cm <sup>2</sup> )	タブレット型洗剤の物性				
	洗剤粒子	水溶性高分子化合物	有機酸	炭酸塩		全空隙率 (%)	マイクロ空隙率 (%)	マクロ空隙率 (%)	圧壊強度(kgf)	溶解時間 (秒)
1	75	3	11	11	10	29	11	18	4.0	150
2	80	4	8	8	15	25	9	16	3.9	200
3	87	5	4	4	20	22	7	15	5.3	230
4	87	5	4	4	15	25	9	16	4.8	210
5	87	5	4	4	10	28	11	17	3.8	210
6	82	8	5	5	15	34	9	25	3.5	140
7	83	7	5	5	15	34	9	25	3.5	140
比較例										
1	95	5	0	0	15	30	16	14	4.5	480
2	85	5	5	5	15	24	16	8	1.5	340
3	87	3	5	5	50	16	8	8	6.8	450
4	87	3	5	5	50	17	8	9	4.6	410
5	85	5	5	5	80	14	5	9	4.2	380

[0103] It turns out that each tablet mold detergent obtained from the result shown in Table 1 in the examples 1-7 dissolves promptly underwater since dissolution time amount is short, and it excels in a mechanical strength in dryness since collapse reinforcement is high.

[0104]

[Effect of the Invention] The tablet mold detergent of this invention is excellent in a mechanical strength in dryness, and has the outstanding property to collapse easily in a damp or wet condition.

Moreover, according to the manufacture approach of this invention, in dryness, it excels in a mechanical strength, and the effectiveness that the macro voidage which collapses easily in a damp or wet condition can manufacture easily 15% or more of tablet mold detergent is done so.

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[Translation done.]

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to a tablet mold detergent and its manufacture approach. It is related with the tablet mold detergent which dissolves promptly, and its manufacture approach in more detail, foaming to carbon dioxide gas underwater.

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[Translation done.]

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PRIOR ART

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[Description of the Prior Art] Conventionally, the tablet mold detergent is manufactured by compression or by carrying out eburnation in detergent powder. since a tablet mold detergent does not have the need for measuring -- handling -- easy -- moreover, \*\* -- since it is not high, there is an advantage that it is compact, and storage space is small and ends.

[0003] However, it does not have mechanical strength sufficient by dryness, but the conventional tablet mold detergent has the fault of collapsing and being hard to dissolve, even if it is a time of getting wet.

[0004] Then, as a tablet mold detergent which can cancel this fault, a carbonate or a bicarbonate, and an organic acid are blended, and when dipped in water, the tablet mold detergent with which the dissolution is promoted is proposed by foaming of carbon dioxide gas (JP,62-30197,A, JP,58-105910,A, JP,62-89616,A).

[0005] However, the tablet mold detergent which blended these carbonates or bicarbonates, and organic acids has the fault that time lag is for water to advance and foam to the interior of a tablet, although a tablet front face contacts water and foams underwater. When a tablet mold detergent contacts water, in order that components, such as an activator, may check gelation thru/or that form a \*\*-strike and water advances [ components, such as this activator gelled thru/or pasted ] into the interior on the front face, the cause requires time amount for the reaction inside a tablet, and is not to fully acquire the effectiveness of promotion of the dissolution by foaming.

[0006] When it fabricates so that it may collapse easily and it may dissolve, and a tablet may have high voidage with low compression moulding pressure even if a front face does not gel underwater or it gels in order to cancel these faults, the tablet mold detergent obtained runs short of mechanical strengths, and has the fault of being inferior to handling nature.

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[Translation done.]



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EFFECT OF THE INVENTION

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[Effect of the Invention] The tablet mold detergent of this invention is excellent in a mechanical strength in dryness, and has the outstanding property to collapse easily in a damp or wet condition. Moreover, according to the manufacture approach of this invention, in dryness, it excels in a mechanical strength, and the effectiveness that the macro voidage which collapses easily in a damp or wet condition can manufacture easily 15% or more of tablet mold detergent is done so.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] So that this invention may be made in view of said conventional technique, an organic acid may be mixed with a carbonate or a bicarbonate in a tablet mold detergent and a carbonate or a bicarbonate, and an organic acid may react promptly also inside a tablet (foaming) It aims at offering the tablet mold detergent which the dissolution was promoted by foaming of carbon dioxide gas when dipped in water by giving high voidage so that water might advance easily underwater, and was excellent in the mechanical strength in dryness.

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[Translation done.]

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